

APPLICATION OF INVERSE PROBLEM AND THERMOGRAVIMETRY TO DETERMINE THE KINETICS OF OIL SHALE PYROLYSIS

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Abstract. For the optimal design of different reactors using fuel particles, it is necessary to know the effect of chemical mechanism on physical properties and thermal heat transfer. Thus, mathematical models that describe the reaction scheme happening in the thermochemical conversions, as well as methods to estimate the Arrhenius parameters for chemical reactions are objects of study. This paper proposes a reactionary scheme to oil shale pyrolysis, where the kinetics parameters are estimate using the Levenberg-Marquardt method of minimization of the ordinary least square norm. A code developed under the MATHEMATICA platform is developed to solve the partial differential equations system as well as the solution of the inverse problem of parameter estimation.

Keywords: oil shale combustion, kinetic model, Levenberg-Marquardt, parameter estimation, inverse problem

1. INTRODUCTION

In the thermal degradation of the solid fuels, the kinetic parameters estimation is extremely important to build the reaction schemes. For the complex reaction mechanism involving various simultaneous reactions, a robust numerical procedure may be used.

Various methods to estimate kinetic parameters are available (Ozawa 1965), (Park and Froment 1998), (Kissinger 1957). Some of them provide relatively net information about mass loss behavior, but calculation of kinetic parameters are based on the ordinary assumptions do not correspond to the complex chemical reactions during the thermal degradation (Kök and Pamir 2000). As example the graphical method (Kissinger 1957), (Ozawa 1965), and numerical fitting (Gal, Soper et al. 1972), (Horgan 1974) are limited only to one overall reaction. In the case of simultaneous reactions, a numerical procedure may be used, i.e. genetic algorithms (Rein, Lautenberger et al. 2006) and inverse problem algorithm (Loulou, Salvador et al. 2003), (Reverte, Dirion et al. 2007).

An inverse problem occurs in many branches of science (Özisik and Orlande 2000), (Dantas, Orlande et al. 2003), (Colombo 2007) where the values of some model parameter must be obtained from the observed data. Here Thermogravimetric Analysis (TGA) is used as experimental data. TGA is an analytical technique used to determine changes in weight in relation to change in temperature. The difference in temperature between the sample and a reference material is recorded while both are subjected to the same heating programme. Thus, the present parameter estimation problem is solved with Levenberg-Marquardt's method by using TG data to estimate the Arrhenius parameters of the reactions present in the pyrolysis process.

(Loulou, Salvador et al. 2003) proposed the kinetics parameters estimation of cardboard pyrolysis by inverse problems using measurements collected from TGA. The kinetic model of cardboard decomposition, Eq. (1), proposed by (David, Salvador et al. 2003) is present follow,



where the cardboard is converted into an intermediate pseudo-species and the pseudo-species are converted into char.

(Reverte, Dirion et al. 2007) describes additional numerical techniques to help to determine the kinetic parameters and to design a more robust parameter estimation tool using the kinetic model proposed by (Bradbury, Sakai et al. 1979), presents in the Eq. (2) and Eq. (3) as follows,



where, G_1 are the gaseous products and G_2 are the other gases.

For the present work oil shale was used as fuel particle to perform the pyrolysis process. Oil shales consist of a mineral porous matrix with the porosity filled with oil, called kerogen, representing 10–65% of the total mass. The mineral matrix consists of carbonates, quartz and clay (Saoiabi, Doukkali et al. 2001). Due to its complex composition when submitted under higher temperatures a lot of complex and parallel reactions takes places. The oil shale dries when it is heated. The organic fraction then devolatilizes and produces volatile matter. Part of this volatile matter will condense to form liquid oil. A solid residue called fixed carbon is left in the mineral matrix. If the temperature is high, the carbonates in the oil shale are decarbonated, either partly or totally, (Martins, Salvador et al. 2010).

For all reactions mechanism, the Arrhenius equation, Eq. (4), indicates the rate of chemical reactions for each species,

$$k_i = A_i \exp\left(-\frac{E_i}{RT}\right) \quad \text{with } (i = 1, 2, \dots, 6) \quad (4)$$

where k is the Arrhenius constant, A is the pre-exponential factor, E is the activation energy, R is the ideal gas constant and T is the temperature. The subscript i indicates the number of chemical species.

To obtain a better understanding of the kinetics of oil shale pyrolysis process, the following aims were formulated to this work:

- To formulate a numerical procedure based on the inverse problem algorithm to estimate the Arrhenius parameters;
- To develop a code under the MATHEMATICA 7.0 platform to solve the partial differential equations system as well as the solution of the inverse problem of parameter estimation.

The numerical modeling of the Arrhenius equation requires the accurate knowledge of pre-exponential factor and the activation energy, both parameters that appear in the formulation. The identification of such parameters from the knowledge of mass loss measurements for each species is an *Inverse Problem*. Generally, inverse problems are mathematically classified as *ill-posed*, in the sense that their solutions do not satisfy Hadamard's requirement of stability under small perturbations in the input data (Dantas, Orlande et al. 2002). Despite the ill-posed character, the solution of an inverse problem can be obtained through its reformulation in terms of a well-posed problem, such as a minimization problem associated with some kind of regularization (stabilization) technique. Different methods based on such an approach have been successfully used in the past for the estimation of parameters and functions, in linear and non-linear inverse problems. They include the Levenberg-Marquardt method of parameter estimation (Dantas, Orlande et al. 2002).

2. COMPOSITION AND THERMOCHEMICAL ANALYSIS OF OIL SHALE

The Thermogravimetric experiment adopted was used by (Martins, Salvador et al. 2010) for oil shale pyrolysis. The author used the oil shale layer of Timahdit in Morocco, where its overall composition is present in Tab. 1.

Table 1. Overall composition of the Timahdit oil shale.

Composition	Present Work (%)
Water	0.99
Organic Matter	17.01
Carbonates ($CaCO_3$)	34.60
Inert Material	47.40

2.1. ThermoGravimetric Analysis (TGA)

The TGA experiments were carried out using a TG – DSC 111 (Setaram) with the very sensitivity microbalance (limit of detection: 1µg). The temperature measurements were reproducible within ± 0.1 K at a temperature scale uncertainty ± 0.5 K. The samples with 40 mg approximately were heated at a heating rate of 10 K/min up to 800°C. Figure 1 shows the pyrolysis of oil shale sample under nitrogen. TG experiments were repeated and show a good reproducibility, with a maximum deviation of a few % wt.

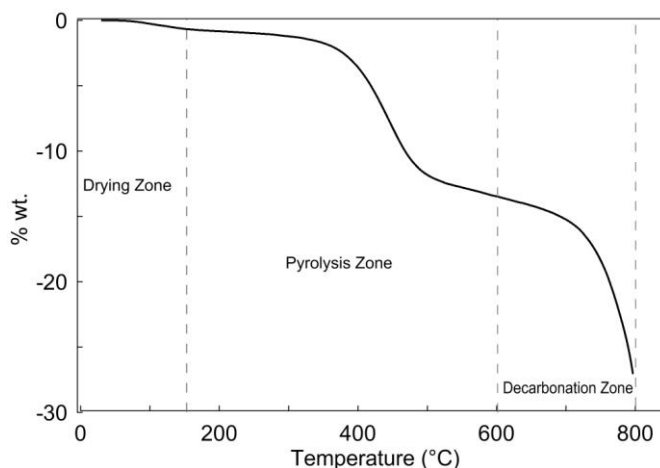


Figure 1. TGA of oil shale under nitrogen – heating rate a 10 k min^{-1} , (Martins, Salvador et al. 2010).

As knowing the presence of a wide variety of minerals in the oil shale matrix significantly complicates thermal behavior, consequently, a diversity of reactions is brought about by the application of heat on the oil shale samples. In general, the following reactions can be identified:

- (a) evolution of water and gases;
- (b) conversion of kerogen to bitumen;
- (c) alteration of bitumen;
- (d) dissociation of bitumen from oils, gases and other compounds;
- (e) vaporization of oils;
- (f) burn-off of fixed carbon;
- (g) decomposition of organic residues and inorganic minerals.

In decomposition of the oil shale sample, as shown in Fig.1, several stages are indicated:

(a) at temperatures between 50 and 150 °C a mass loss of a few %wt. can be observed. It can be attributed to water evaporation;

(b) in the temperature range 150–600 °C an important mass loss can be observed. The differential scanning calorimetric test performed further, Fig. 2, did not indicate a significant reaction heat. This stage was attributed to organic matter decomposition into volatile matter - including condensable oil - and into solid FC;

(c) in the temperature range 600–800 °C, a last and important mass loss was observed. The differential scanning calorimetric test performed further, Fig. 2 indicated a strongly endothermic reaction. This stage was attributed to the thermal decomposition of carbonates producing carbon dioxide.

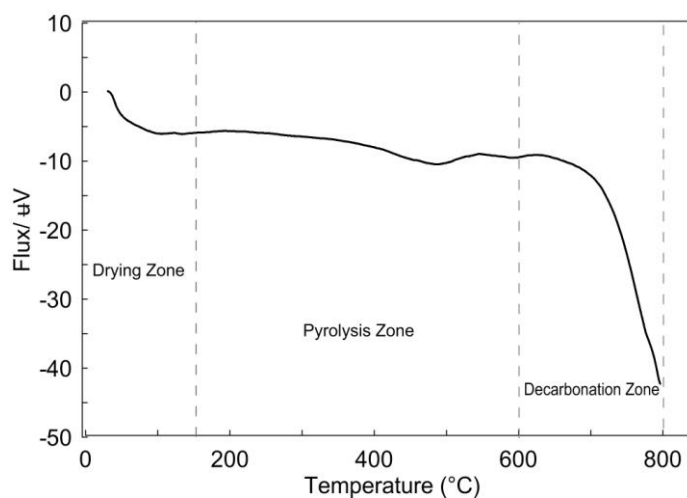


Figure 2. DSC of oil shale under nitrogen – heating rate a 10 k min^{-1} , (Martins, Salvador et al. 2010).

There is no clear separation between the two stages of organic matter decomposition and decarbonation along the test. For this reason, it was difficult to determine with any accuracy the amount of organic matter and carbonates.

2.2. Kinetic Model

The oil shale decomposition is extremely complex because of the presence of parallel and consecutive reactions. This paper proposes a realistic reaction schemes for the oil shale pyrolysis, presented in Eq. (9). The first reaction is the overall reaction of oil shale (OS) decomposition, resulting in Organic Matter (OM), Calcium Carbonates (CaCO₃), water and Inert Material (IM). The second reaction corresponds to the drying of oil shale where water undergoes evaporation at temperature range of 100 - 250 °C. The subsequent reaction involves the devolatilization of organic matter, releasing volatile material (VM) and leaving fixed carbon (FC) in the solid matrix. Finally, thermal decarbonation of CaCO₃ takes place in the temperature range 600 – 800 °C. In the solid residue after combustion remains an inert material.



The stoichiometric coefficients, $\alpha = 0.758$ and $\beta = 0.56$, were determined by (Martins, Salvador et al. 2010). The first order rate equations for the oil shale decomposition, Eq. (10–17), may then be stated as follows:

$$\frac{dY_{H_2O}}{dt} = -k_2 Y_{H_2O} \tag{10}$$

$$\frac{dY_{OM}}{dt} = -k_3 Y_{OM} \tag{11}$$

$$\frac{dY_{VM}}{dt} = (\alpha)k_3 \frac{MW_{VM}}{MW_{OM}} Y_{OM} \tag{12}$$

$$\frac{dY_{FC}}{dt} = (1-\alpha)k_3 \frac{MW_{FC}}{MW_{OM}} Y_{OM} \tag{13}$$

$$\frac{dY_{CaCO_3}}{dt} = -k_4 Y_{CaCO_3} \tag{14}$$

$$\frac{dY_{CaO}}{dt} = (\beta)k_4 \frac{MW_{CaO}}{MW_{CaCO_3}} Y_{CaCO_3} \tag{15}$$

$$\frac{dY_{CO_2}}{dt} = (1-\beta)k_4 \frac{MW_{CO_2}}{MW_{CaCO_3}} Y_{CaCO_3} \tag{16}$$

$$Y = Y_{H_2O} + Y_{OM} + Y_{FC} + Y_{CaCO_3} + Y_{IM} \tag{17}$$

where Y_i is normalized mass of species i , MW is its molar mass. The initial conditions for Eq. (10-16) were: $Y_{H_2O} = 0.0099$, $Y_{OM} = 0.1701$, $Y_{CaCO_3} = 0.346$, $Y_{IM} = 0.474$, $MW_{VM} = 11$ g/mol, $MW_{OM} = 11$ g/mol, $MW_{FC} = 12$ g/mol, $MW_{CaO} = 57$ g/mol, $MW_{CaCO_3} = 101$ g/mol, $MW_{CO_2} = 44$ g/mol.

3. KINETICS PARAMETERS ESTIMATION

For the inverse problem of interest here, the parameters A_i and E_i , $i=1\dots4$, are regarded as unknown quantities for each of Equations (10) to (16). For the estimation of such parameters, we consider available the mass loss

measurements Y_n . The subscript n refers to the time at which the measurements are taken, that is, t_n , for $n=1\dots N$. We note that the mass loss measurements may contain random errors, but all the other quantities appearing in the formulation of the direct problem are supposed to be known exactly.

Inverse problems are *ill-posed* (Dantas, Orlande et al. 2002). Several methods of solution of inverse problems, such as the one used here, involve their reformulation in terms of well-posed minimization problems. By assuming additive, uncorrelated and normally distributed random errors, with constant standard deviation and zero mean, the solution of the present parameter estimation problem can be obtained through the minimization of the ordinary least-squares norm (Dantas, Orlande et al. 2002). Such a norm can be written as

$$S(P) = [Y - M(P)]^T [Y - M(P)] \quad (18)$$

where $P = [A_i, E_i]$, for $i=1\dots 4$, denotes the vector of unknown parameters. The superscript T above denotes transpose and $[Y - M(P)]$ is given by

$$[Y - M(P)]^T = \left[(\bar{Y}_1 - \bar{M}_1), (\bar{Y}_2 - \bar{M}_2), \dots, (\bar{Y}_N - \bar{M}_N) \right] \quad (19)$$

where $(\bar{Y}_N - \bar{M}_N)$ is a row vector containing the differences between the measured and estimated mass loss at the measurement time t_n ,

The present inverse problem of parameter estimation is solved with the Levenberg-Marquardt method of minimization of the least-squares norm. The Levenberg-Marquardt method is quite stable, powerful and straightforward (Özsisik and Orlande 2000), and has been used to a diversity of inverse problems. Eq. (8) shows the iterative procedure of the Levenberg-Marquardt method,

$$P^{(k+1)} = P^{(k)} + [(J^{(k)})^T J^{(k)} + \mu^{(k)} \Omega^{(k)}]^{-1} (J^{(k)})^T [Y - M(P^{(k)})] \quad (20)$$

where P represents the unknowns parameters, the subscript (k) defines the iteration number and J represents the sensitivity matrix. The parameters μ and Ω , respectively, are the damped parameter and damped matrix from Levenberg-Marquardt. This iterative process contains oscillations and instabilities that difficult the convergence process. Thus, the damped parameter is used to minimize these problems and make the convergence faster.

The sensitivity matrix is defined as

$$J = \left[\frac{\partial M^T(P)}{\partial P} \right]^T = \begin{bmatrix} \frac{\partial M_1}{\partial p_1} & \dots & \frac{\partial M_1}{\partial p_m} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \frac{\partial M_N}{\partial p_1} & \dots & \frac{\partial M_N}{\partial p_m} \end{bmatrix} \quad (21)$$

The elements of the sensitivity matrix are the sensitivity coefficients. They are defined as the first derivative of the estimated temperatures with respect to each of the unknown parameters P_m , $m = 1, \dots, M$.

The Levenberg-Marquardt algorithm used in this work was obtained from the built-in function *FindMinimum* of the *Mathematica* software. The stopping criterion used is when either the goals specified by *AccuracyGoal* or *PrecisionGoal* is achieved. *AccuracyGoal* is an option which specifies how many effective digits of accuracy should be sought in the final result and *PrecisionGoal* is an option which specifies how many effective digits of precision should be sought in the final result. In this work, both goals were set to 8, the default value defined by *Mathematica*.

3. RESULTS AND DISCUSSION

3.1. Parameter Estimation

Parameters A_i and E_i estimated with the Levenberg-Marquardt algorithm where obtained for a heat rate of 10K/min. To estimation of A_2 and E_2 , A_3 and E_3 , A_4 and E_4 were made by using 43, 43 and 41, transient mass loss readings respectively. The initial guesses used in the iterative procedure of the Levenberg-Marquardt method where taken as 0.016 s^{-1} for A_2 and 10000 Jxmol^{-1} for E_2 , 1.6 s^{-1} for A_3 and 39500 Jxmol^{-1} for E_3 , 400000 s^{-1} for A_4 and $176400 \text{ Jxmol}^{-1}$

for E_4 . These values adopted were chosen by comparing to values found to the similar reactions available in the literature.

The oil shale sample, in drying zone, lost a small amount of water. This reaction occurs in a time range of 0-1200 s and the Arrhenius parameters estimated were $E_2= 19.87 \text{ kJ mol}^{-1}$ and $A_2=0.851 \text{ s}^{-1}$. In the time range of 1200-3400 s, the activation energy and pre-exponential factor found for pyrolysis zone were $E_3= 79.76 \text{ kJ mol}^{-1}$ and $A_3=1616 \text{ s}^{-1}$ and the interval between 3200-4400 s, the Arrhenius parameters found were $E_4= 196.54 \text{ kJ mol}^{-1}$ and $A_4=1.09 \times 10^7 \text{ s}^{-1}$ for the decarbonation zone. Table 2 presents the Arrhenius parameters estimated in this work.

Table 2. Results for parameters estimation for oil shale pyrolysis.

Parameters	Estimated	Standard Deviation	Error (%)
$A_2 \text{ (s}^{-1}\text{)}$	8.61E-01	2.22E-04	0.00
$E_2 \text{ (J x mol}^{-1}\text{)}$	19.95E+03	1.95E+02	2.50
$A_3 \text{ (s}^{-1}\text{)}$	16.42E+02	7.69E-03	0.00
$E_3 \text{ (J x mol}^{-1}\text{)}$	79.94E+03	5.16E+01	0.01
$A_4 \text{ (s}^{-1}\text{)}$	1.11E+07	0.40E+01	0.00
$E_4 \text{ (J x mol}^{-1}\text{)}$	196.84E+03	6.55E+01	0.00

Table 3 presents the parameters estimated in this work compared with results found in literature. One can see that despite a discrepancy between the values found for several authors, the results obtained herein are in good agreement with the literature.

Table 3. Activation energy and pre-exponential factor for oil shale pyrolysis.

Literature	Drying Zone		Pyrolysis Zone		Decarbonation Zone	
	$E(\text{kJ mol}^{-1})$	$A(\text{s}^{-1})$	$E(\text{kJ mol}^{-1})$	$A(\text{s}^{-1})$	$E(\text{kJ mol}^{-1})$	$A(\text{s}^{-1})$
(Present Work)	19.87	8.51E-01	79.76	16.16E+02	196.54	1.09E+07
(Sonibare, Ehinola et al. 2005)	—	—	75.0	3.95E-01	—	—
(Kök and Pamir 1999)	—	—	53.1	0.94E+01	—	—
(Kök, Sztatisz et al. 1999)	—	—	46.0	8.1E-03	—	—
(Galwey and Brown 1997)	—	—	—	—	205.00	—
(Liu and Zhang 2003)	—	—	—	—	215.00	—
(Martins, Salvador et al. 2010)	—	—	—	—	135.00	4.46E+02

4. CONCLUSION

A numerical routine to estimate the kinetics of thermochemical degradation for solid fuels was developed with successes. This routine applies both inverse problem and TGA experiments to propose new reaction mechanism. Here, oil shale kinetics was established and its parameters estimated with accuracy, with a maximum deviation of a few%.

By exploiting the TG data, it was established that the oil shale sample contains 0.98% moisture and produced 12.13% VM when heated from 150 to 600 °C. The oil shale also contains 47.40% of inert materials and 34.60% carbonates which produced 15.9 % of CO_2 . Some of these values were used as initial conditions in the system equations and showed be good in the system solution approach.

The estimated parameters A_i and E_i are in good agreement with the ones found in the literature.

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